Non-alkaloidal Bases from Pyrolysis Of Tobacco Leaf Pigment at the Approximate Burn Temperature Of a Cigarette

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By fusing pigment obtained from either tobacco smoke or leaf with potassium hydroxide and examining the bases thus produced, Dymicky and co-workers implicated certain alkaloids and simple pyridines in the structural make-up of pigment (2, 3). Their reports prompt us to record the formation of similar and related bases from the pyrolysis of tobacco leaf pigment which we observed initially during the course of experiments on the pyrolytic formation of phenols from such pigment (6). That leaf pigment may serve as a potential precursor of pyridine bases found in cigarette smoke has heretofore not been demonstrated. The present report presents preliminary data on the effect of pyrolytic temperature on the base composition of the pyrolysate from leaf pigment. Most striking is the apparent absence of alkaloids in products obtained from the pyrolysis of pigment at a temperature approximating that of the combustion zone of a burning cigarette (8), and the analogous results obtained by subjecting tobacco itself to the same pyrolytic conditions.

Experimental

The isolation and characterization of the Turkish tobacco pigment used in the present study have been detailed (1).

Pyrolyses of either pigment or tobacco (Turkish) were performed in a stream of nitrogen (30 ml/min) utilizing techniques and apparatus described previously (6). For the bulk of the data presented in the present report, pyrolyses were conducted at a temperature of 857 ±3°C to closely approximate the reported burn temperature of a cigarette (8). For proper perspective, however, several studies were undertaken at somewhat lower temperatures.

The basic fractions from pyrolysates were obtained ultimately in diethyl ether solution and examined by gas chromatography as described (7).

Levels of bases in pyrolysates were determined by the usual gas chromatographic peak area measurements.

Results and Discussion

The principal bases obtained from the pyrolysis of Turkish tobacco pigment (857°C, N_2), and their yields, are shown in **Table 1**. For comparative purposes, similar data obtained by pyrolyzing Turkish tobacco under identical conditions are included. In either case, the gas chromatograms from which the data were derived were quite similar to the chromatogram of the basic fraction from cigarette smoke condensate (7), and therefore large peaks in the area of nicotine elution were assumed initially to be alkaloidal in nature. Although cochromatography of the basic fractions from pyrolysates with known bases helped to verify the presence of pyridine and simple pyridine derivatives among the pyrolytic products, it gave no evidence to indicate the presence of nicotine and other alkaloids. Subsequent ultraviolet spectral analysis indicated that the two major peaks, eluting in the nicotine region, were quinoline and isoquinoline respectively. The presence of alkaloids could not be demonstrated in pyrolysates from either pigment or leaf pyrolyzed at a temperature of 857°C.

The results of Dymicky *et al.* (2, 3) would lead one to expect nicotine and related alkaloids in pigment pyrolysates. Similarly, in view of the base composition of cigarette smoke condensate (7), one would expect a high proportion of nicotine in tobacco pyrolysates. The observation that pyrolysis of pigment or tobacco at temperatures approximating that of a burning cigarette produces little if any nicotine indicates that nicotine is highly susceptible to pyrolytic destruction, as implied previously in the literature (4, 5, 9). More significantly, the present data point up the difficulties likely to be encountered in

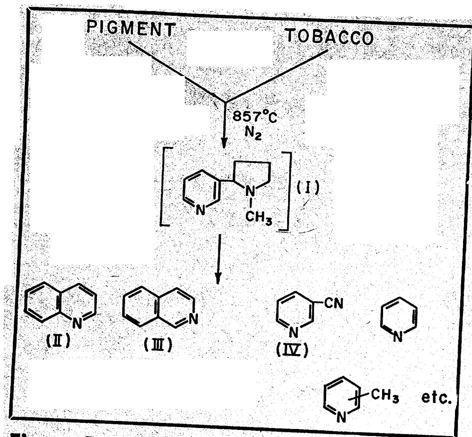

Figure 1. Bases from pyrolysis of tobacco and pigment.

Table 1. Bases from pyrolysis of Turkish tobacco and Turkish tobacco pigment (857° C, N_2)

Base	Yield (mg/100 g pyrolyzed) Leaf	Pigment
Pyridine	39	36
α-Picoline	5	14
β-, γ-Picoline	11	22
2,4-, 2,5-Lutidine		
2,3-Lutidine Collidine	—	5
3-Ethyl pyridine	2	1
3,5-Lutidine	<1	<1
3-Vinyl pyridine 3,4-Lutidine	8	5
Nicotinonitrile	11	28
Quinoline	45	44
Isoquinoline	26	31

trying to replicate by means of simple pyrolysis studies the conditions that are characteristic of a burning cigarette. In the present study, it seems likely that any nicotine (I) produced (or liberated) initially by pyrolytic action is subsequently subjected to secondary pyrolytic effects and converted mainly to quinoline (II), isoquinoline (III), nicotinonitrile (IV) and simple pyridines (**Figure 1**). In contrast to the experimental condition used in the present study, a burning cigarette is characterized by a temperature gradient; within the range of that gradient, at least two chemical processes may be in operation, namely pyrolysis and distillation. In a burning cigarette, depending upon the temperature in a given region, nicotine may be subjected to either of the two processes. The nicotine that is distilled finds its way into the smoke as nicotine; that which is pyrolyzed manifests itself as pyridine, simple pyridine derivatives, nicotinonitrile, quinoline and isoquinoline.

Not unexpectedly, relatively small amounts of nicotine and nornicotine were obtained when pigment or tobacco was pyrolyzed at 700°C. In the case of tobacco, the level of nicotine in the pyrolysate increased progressively as the temperature of pyrolysis was lowered (to 300°C).

In view of the alkaline fusion (2, 3) and pyrolysis studies, it is tempting to speculate on the nature of the chemical linkage that bonds the bases within the pigment. The tertiary character of these amines generally implicated in pigment structure suggests that they are bonded to acid groups within the pigment through complex salt linkages involving nitrogen. The alkaline fusion, therefore, may effect hydrolysis initially and distillation of the liberated bases subsequently. On the other hand, in the pyrolysis studies at high temperatures, distillation effects are virtually absent. The degree of distillation as opposed to pyrolysis would then explain the differences in the relative levels of nicotine in the respective studies (fusion vs. pyrolysis).

Additional experiments related to pyrolytic temperature and product composition are currently in progress.

Summary

Tobacco leaf pigment pyrolyzed in a stream of nitrogen (30 ml/min) and at the approximate burn temperature of a cigarette produced a number of non-alkaloidal bases including quinoline, isoquinoline, nicotinonitrile, pyridine and simple pyridine derivatives. The base composition of the pyrolysate was shown to be a function of temperature. Tobacco showed pyrolytic properties similar to those of pigment.

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